Europäisches Patentamt

European Patent Office

Office européen des brevets



EP 0 709 225 B1 (11)

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent: 05.08.1998 Bulletin 1998/32

(51) Int. Cl.⁶: **B41M 5/28**, B41M 5/34

(21) Application number: 95307663.5

(22) Date of filing: 27.10.1995

(54) Reversible multi-color thermal recording medium

Reversibles mehrfarbiges wärmeempflindliches Aufzeichnungsmaterial Matériau pour l'enregistrement thermique multicolore et réversible

(84) Designated Contracting States: BE DE FR GB IT SE

(30) Priority: 27.10.1994 JP 262998/94 29.11.1994 JP 294142/94

(43) Date of publication of application: 01.05.1996 Bulletin 1996/18

(73) Proprietor: NIPPON PAPER INDUSTRIES CO., LTD. Kita-ku, Tokyo (JP)

(72) Inventors:

 Minami, Toshiaki, c/o Res. Lab. of Product Dev. 1-chome, Shinjuku-ku, Tokyo 161 (JP)

· Nagai, Tomoaki, c/o Res. Lab. of Product Dev. 1-chome, Shinjuku-ku, Tokyo 161 (JP)

· Hamada, Kaoru, c/o Res. Lab. of Product Dev. 1-chome, Shinjuku-ku, Tokyo 161 (JP) · Sekine, Akio, c/o Res. Lab. of Product Dev. 1-chome, Shinjuku-ku, Tokyo 161 (JP)

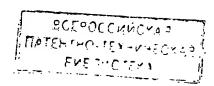
(74) Representative: **Woods, Geoffrey Corlett** J.A. KEMP & CO. 14 South Square Gray's Inn London WC1R 5LX (GB)

(56) References cited:

EP-A- 0 530 699

US-A-5168029

- PATENT ABSTRACTS OF JAPAN vol. 18 no. 383 (M-1640) ,19 July 1994 & JP-A-06 106844 (TOPPAN PRINTING COMPANY LIMITED) 19 April 1994,
- PATENT ABSTRACTS OF JAPAN vol. 18 no. 383 (M-1640) ,19 July 1994 & JP-A-06 106849 (MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED) 19 April 1994,



Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

10

25

30

35

In the above formula, X, R1, R2, R3, R4, R5, R6, R7 and R8 are independently selected from the group consisting of a lower alkyl group having 1 to 6 carbon atoms, alkoxy group having 1 to 6 carbon atoms, hydrogen atom, nitro group, cyano group and halogen atom, and m is an integer of 1 to 3.

$$\begin{array}{c} X \\ NH - C - NH - (CH_2) \\ M \end{array} = NH - C - NH - \begin{array}{c} X \\ M \\ OH \end{array} \qquad \cdots \qquad (IV)$$

In the above formula, X is selected from the group consisting of a lower alkyl group having 1 to 6 carbon atoms, alkoxy group having 1 to 6 carbon atoms, nitro group, halogen atom and hydrogen atom, m is an integer of 1 to 12, and n is an integer of 1 or 2.

$$x_{n} = \underbrace{\begin{array}{c} 0 \\ \parallel \\ -NH - C - NH - C \\ \end{array}}_{R_{1}} = \underbrace{\begin{array}{c} R_{3} \\ R_{2} \end{array}}_{R_{2}} = \underbrace{\begin{array}{c} (V) \\ -NH - C \\ \end{array}}_{R_{1}}$$

In the above formula, X is selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, alkoxy group having 1 to 12 carbon atoms, trihalogenated methyl group, hydrogen atom, nitro group and halogen atom, Z is selected from the group consisting of O, S, straight chain having 1 to 12 carbon atoms, branched chain C_1 - C_{12} alkylene group, NH, SO $_2$ and C=O, R1, R2 and R3 are independently selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, hydrogen atom, nitro group and halogen atom, and n is an integer of 1 to 3.

As for erasure of an image on the reversible thermal recording medium, various methods are conceivable such as one in which temperature and the amount of heat lower than those at the time of recording are given with a thermal head, a hot stamp, a heated roll or the like for erasure, one in which the amount of light smaller than that at the time of recording is irradiated by a laser, a halogen lamp or the like for erasure, and one in which the ground of a recording medium is brought into contact with a low-boiling alcohol solvent such as methanol and ethanol for erasure. Particularly, a heated roll controlled to 100 to 150 °C is easily used from a view point of operational ease. In this case, since the reversible recording composition and the irreversible recording composition are treated with a heated roll at the same time, a heat-resistant color developer needs to be used to prevent both of the reversible recording composition and the irreversible recording composition from developing colors from their grounds.

Further, as for the order of laminating the reversible recording composition and the irreversible recording composition onto a substrate, the substrate, the irreversible recording composition and the reversible recording composition may be laminated in the order named, or the substrate, the reversible recording composition and the irreversible recording composition may be laminated in the order named. Or two or more layers of the reversible recording composition and the irreversible recording composition may be laminated together.

In the present invention, since the hue of an image obtained by first recording or erasure is made different from the

EP 0 709 225 B1

$$M \in O \longrightarrow -N \parallel -C - N \parallel -C - N$$

$$R_{3} = n-Buty1$$

$$R_{2} \stackrel{\text{O}}{\longrightarrow} NII - C - NII - (CII_{2}) \stackrel{\text{O}}{\circ} - NII$$

$$C = O$$

$$R_{2} = n \cdot \text{llexyl}$$

$$R_{2} \stackrel{\text{O}}{\longrightarrow} - NII$$

$$R_{3} \stackrel{\text{O}}{\longrightarrow} - NII$$

$$O_{2} \stackrel{OII}{N} \stackrel{O}{\longrightarrow} -NII - \stackrel{C}{\longrightarrow} -NII - \stackrel{O}{\longrightarrow} -NII - \stackrel{O$$

$$O_{2} N \xrightarrow{OH} C - NH - (CH_{2})_{6} - NH$$

$$C = O$$

$$O_{2} N \xrightarrow{OH} O_{1}$$

$$O_{3} N \xrightarrow{OH} O_{1}$$

$$O_{4} N \xrightarrow{OH} O_{1}$$

$$O_{5} N \xrightarrow{OH} O_{1}$$

$$O_{6} N \xrightarrow{OH} O_{1}$$

$$O_{1} N \xrightarrow{OH} O_{2}$$

$$\begin{array}{c|c}
O_2 & N & O \\
II & O & O \\
II & O$$

$$CI = \begin{pmatrix} OII & O & & O & IIO \\ & & & & & & & & & & & & & & & \\ & & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$$

EP 0 709 225 B1

EP 0 709 225 B1

1 to 4 or an optical recording medium as defined in claim 6.

Patentansprüche

10

15

20

25

30

35

40

45

50

55

1. Reversibles thermisches Mehrfarben-Aufzeichnungsmedium, das, laminiert auf ein Substrat, umfaßt:

5

(i) eine irreversible thermische Zusammensetzung, umfassend einen farblosen oder blassen, basischen achromatischen Farbstoff und einen organischen, irreversiblen, hitzebeständigen Farbentwickler; und

10

(ii) eine reversible thermische Zusammensetzung, umfassend einen farblosen oder blassen basischen, achromatischen Farbstoff und einen organischen, reversiblen, wärmebeständigen Farbentwickler.

•

2. Aufzeichnungsmedium nach Anspruch 1, weiterhin eine zwischen den Aufzeichnungsschichten, die die thermischen Zusammensetzungen (i) und (ii) umfassen, angeordnete Zwischenschicht umfassend.

15

3. Aufzeichnungsmedium nach Anspruch 1 oder 2, wobei der reversible, wärmebeständige Farbentwickler die folgende Formel (I) besitzt:

20

25

worin X ausgewählt ist aus Wasserstoff, C_1 bis C_{12} Alkyl, Halogen C_1 bis C_3 Alkyl, C_1 bis C_{12} Alkoxy, C_1 bis C_{12} Alkoxy, C_1 bis C_{12} Dialkylamino, Nitro, Cyano, und Halogen, m eine ganze Zahl von 1 bis 12 ist und n eine ganze Zahl von 1 bis 3; oder die folgende allgemeine Formel (I'):

30

35

$$R-NH-C-NH$$
 OH (I')

40

worin R C_{12} bis C_{22} Alkyl ist, A ausgewählt aus Niederalkyl, Niederalkoxy, Niederalkoxycarbonyl, Nitro, Halogen und Wasserstoff und n eine ganze Zahl von 1 bis 3 ist.

5.

4. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 3, wobei der irreversible, wärmebeständige Farbentwickler eine aus den folgenden Formeln (II), (III), (IV) und (V) ausgewählte Struktur besitzt:

45

$$X_m$$
 $N-C-N$
 $N-C-N$

7.

50

6.

worin X ausgewählt ist aus C_1 bis C_4 Alkyl, C_1 bis C_3 Alkoxy, Wasserstoff, Nitro, Cyano und Halogen, und m eine ganze Zahl von 1 bis 3 ist.

55 8.

Claims

- 1. A reversible multi-color thermal recording medium which comprises, laminated on a substrate:
- (i) an irreversible thermal composition comprising a colorless or pale basic achromatic dye and an organic irreversible heat-resistant color developer; and
- (ii) a reversible multi-color thermal composition comprising a colorless or pale basic achromatic dye and an organic reversible heat-resistant color developer.
- 2. A recording medium according to claim 1, which further comprises an intermediate layer interposed between recording layers which comprise the thermal compositions (i) and (ii).
- 3.A recording medium according to claim 1 or 2, wherein the reversible heat-resistant color developer has the following formula (I):

wherein X is selected from hydrogen, C1-C12 alkyl, halo-C1-C3 alkyl, C1-C12 alkoxy, C1-C12 alkoxycarbonyl, C1-C12 acyl, C1-C12 dialkylamino, nitro, cyano and halogen, m is an integer of 1 to 12 and n is an integer of 1 to 3; or the following general formula (I'):

wherein R is C12-C22 alkyl, A is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, nitro, halogen and hydrogen, and n is an integer of 1 to 3.

4.A recording medium according to any one of claims 1 to 3 wherein the irreversible heat-resistant color developer has a formula selected from the following formulae (II), (III), (IV) and (V):

wherein X is selected from C1-C4 alkyl, C1-C3 alkoxy, hydrogen, nitro, cyano and halogen, and m is an integer of 1 to 3;

wherein each of X, R1, R2, R3, R4, R5, R6, R7 and R8, which are the same or different, is independently selected from C1-C6 alkyl, C1-C6 alkoxy, hydrogen, nitro, cyano and halogen, and m is an integer of 1 to 3;

wherein X is selected from C1-C6 alkyl, C1-C6 alkoxy, nitro, halogen and hydrogen, m is an integer of 1 to 12 and n is 1 or 2;

wherein X is selected from C1-C12 alkyl, C1-C12 alkoxy, trihalomethyl, hydrogen, nitro and halogen, Z is selected from O, S, straight chain C1-C12 alkylene, branched chain C1-C12 alkylene, NH, SO2 and C=O, each of R1, R2 and R3, which are the same or different, is independently selected from C1-C6 alkyl, hydrogen, nitro and halogen, and n is an integer of 1 to 3.

- 5. A reversible multi-color thermal recording medium obtainable by laminating a plastic film on a recording medium as defined in any one of the preceding claims, either on the recording surface thereof or on the entire recording medium after thermal recording has occurred.
- 6. A reversible multi-color optical recording medium which comprises, in a recording layer of a recording medium as defined in any one of claims 1 to 4, a light absorbent for absorbing light and converting it into heat.
- 7. An optical recording medium obtainable by laminating a plastic film on a reversible multi-color optical recording medium as defined in claim 6, either on the recording surface thereof or on the entire recording medium.
- 8. An optical recording medium obtainable by laminating a plastic film on a reversible multi-color

optical recording medium as defined in claim 6, either on the recording surface thereof or on the entire recording medium after thermal recording or optical recording has occurred.

- 9. A method of optical recording, which method comprises applying flash light from a stroboscope or laser light to an optical recording medium as defined in claim 7 or 8.
- 10. A sheet suitable for an electronic photocopier, which comprises a recording medium as defined in any one of claims 1 to 4 or an optical recording medium as defined in claim 6.

Data supplied from the esp@cenet database - I2

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:
BLACK BORDERS
☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
☐ FADED TEXT OR DRAWING
☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
☐ SKEWED/SLANTED IMAGES
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
☐ GRAY SCALE DOCUMENTS
☐ LINES OR MARKS ON ORIGINAL DOCUMENT
☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

IMAGES ARE BEST AVAILABLE COPY.

☐ OTHER: _

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.